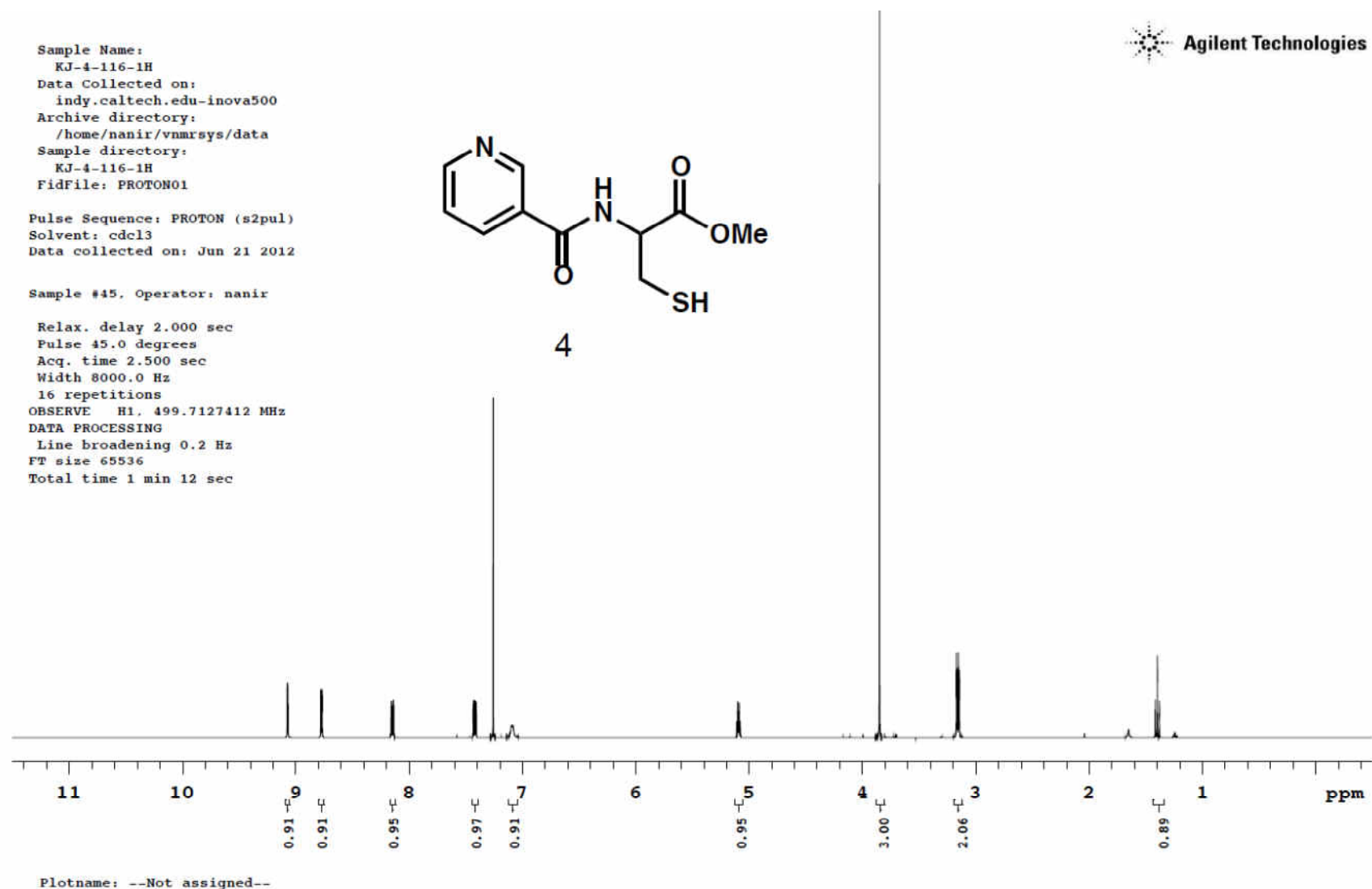


## **Analytical and Bioanalytical Chemistry**

### **Electronic Supplementary Material**

#### **A cationic cysteine-hydrazide as an enrichment tool for the mass spectrometric characterization of bacterial free oligosaccharides**

Kyoung-Soon Jang, Roger R. Nani, Anastasia Kalli, Sergiy Levin, Axel Müller, Sonja Hess, Sarah E. Reisman, William M. Clemons, Jr.



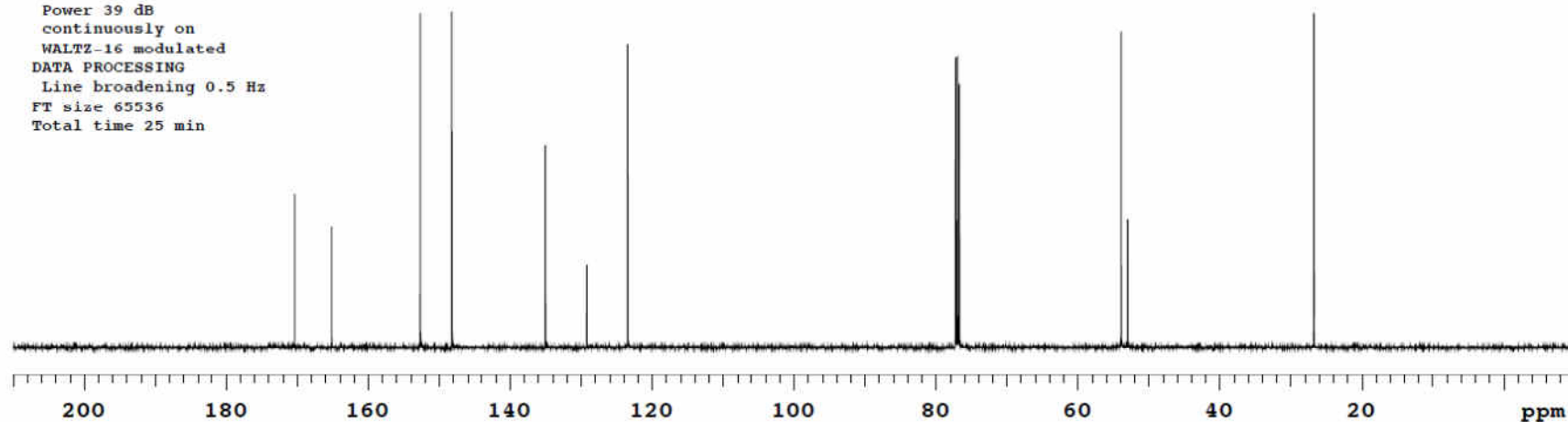
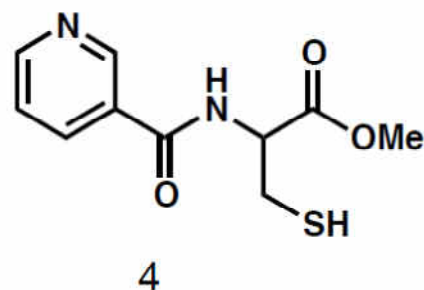
**Fig. S1** NMR spectra of cysteine methyl ester nicotinamide

Sample Name:  
KJ-4-116-13C  
Data Collected on:  
indy.caltech.edu-inova500  
Archive directory:  
/home/nanir/vnmrsys/data  
Sample directory:  
KJ-4-116-13C  
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: Jun 21 2012

Sample #45, Operator: nanir

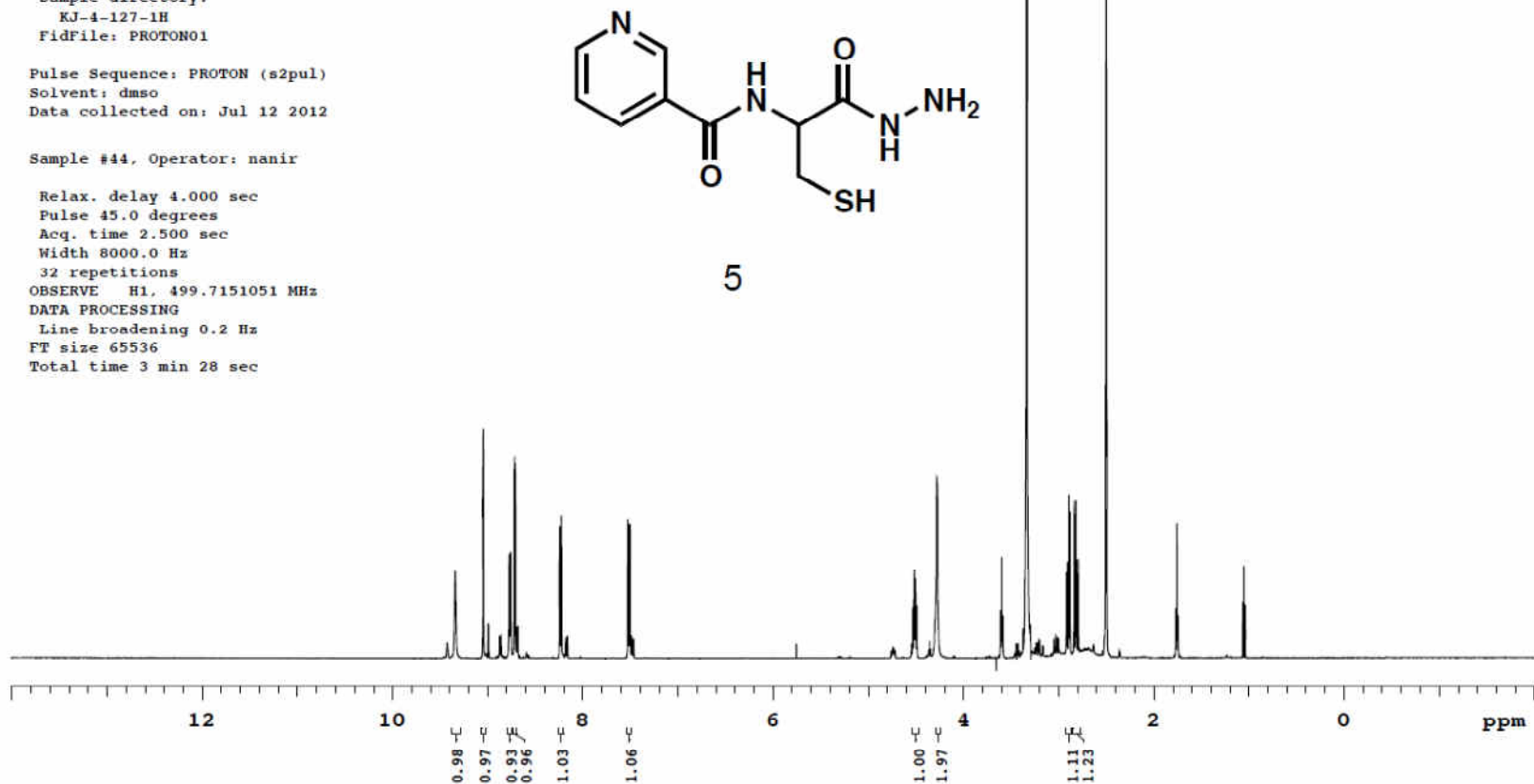
Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 2.000 sec  
Width 31446.5 Hz  
512 repetitions  
OBSERVE C13, 125.6528748 MHz  
DECOUPLE H1, 499.7152303 MHz  
Power 39 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 25 min



Plotname: --Not assigned--

**Fig. S1** (continued) NMR spectra of cysteine methyl ester nicotinamide

Sample Name:  
 KJ-4-127-1H  
 Data Collected on:  
 indy.caltech.edu-inova500  
 Archive directory:  
 /home/nanir/vnmrsys/data  
 Sample directory:  
 KJ-4-127-1H  
 FidFile: PROTON01  
  
 Pulse Sequence: PROTON (s2pul)  
 Solvent: dms0  
 Data collected on: Jul 12 2012  
  
 Sample #44, Operator: nanir  
  
 Relax. delay 4.000 sec  
 Pulse 45.0 degrees  
 Acq. time 2.500 sec  
 Width 8000.0 Hz  
 32 repetitions  
 OBSERVE H1, 499.7151051 MHz  
 DATA PROCESSING  
 Line broadening 0.2 Hz  
 FT size 65536  
 Total time 3 min 28 sec



Plotname: --Not assigned--

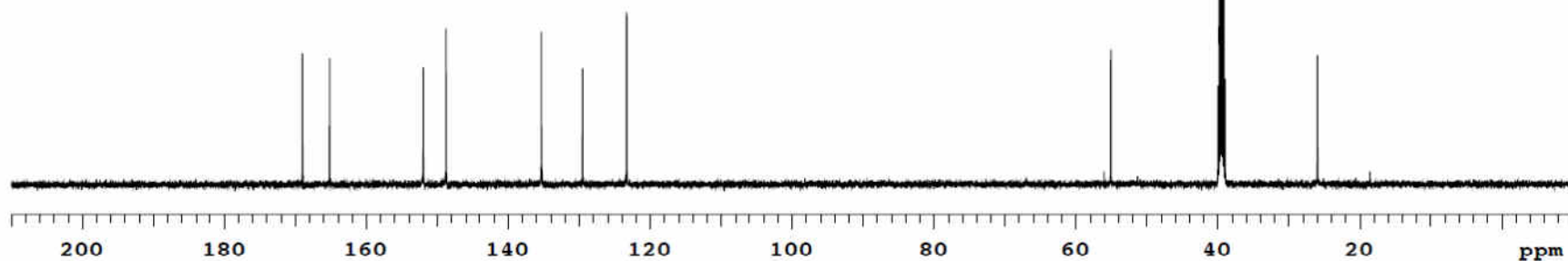
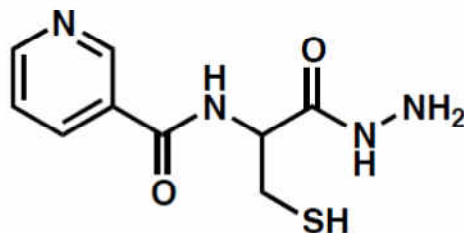
**Fig. S2** NMR spectra of cysteine hydrazide nicotinamide

Sample Name:  
KJ-4-127-13C  
Data Collected on:  
indy.caltech.edu-inova500  
Archive directory:  
/home/nanir/vnmrsys/data  
Sample directory:  
KJ-4-127-13C  
FidFile: CARBON01

Pulse Sequence: CARBON (s2pul)  
Solvent: dmsc  
Data collected on: Jul 12 2012

Sample #45, Operator: nanir

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.800 sec  
Width 31446.5 Hz  
512 repetitions  
OBSERVE C13, 125.6535187 MHz  
DECOUPLE H1, 499.7176040 MHz  
Power 39 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 23 min



Plotname: --Not assigned--

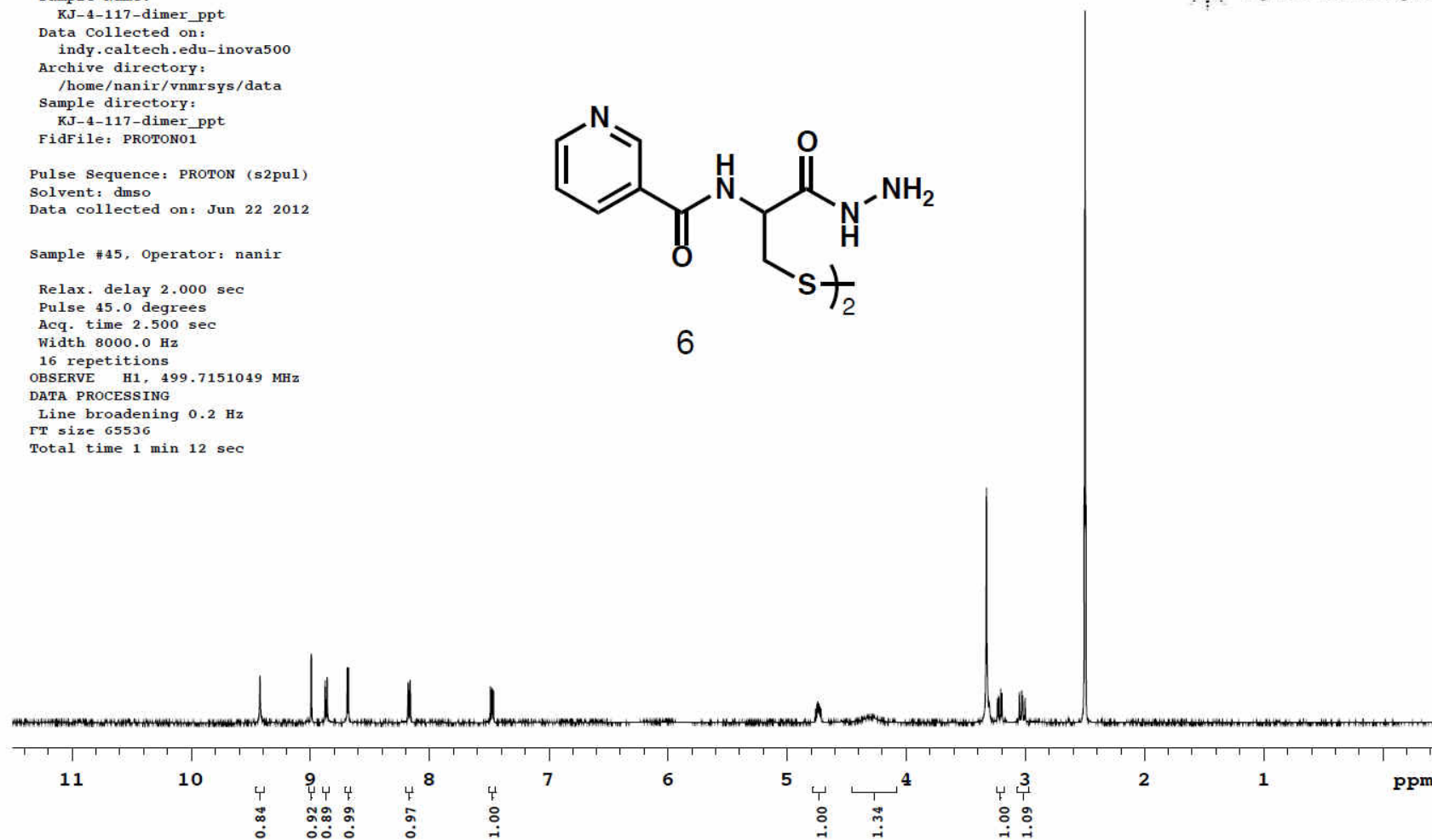
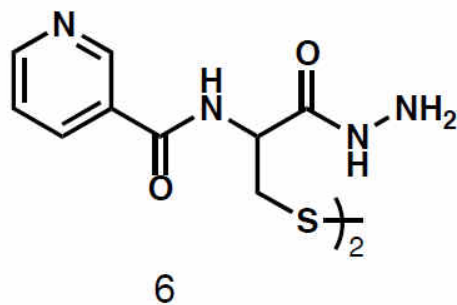
**Fig. S2** (continued) NMR spectra of cysteine hydrazone nicotinamide

Sample Name:  
KJ-4-117-dimer\_ppt  
Data Collected on:  
indy.caltech.edu-inova500  
Archive directory:  
/home/nanir/vnmrsys/data  
Sample directory:  
KJ-4-117-dimer\_ppt  
FidFile: PROTON01

Pulse Sequence: PROTON (s2pul)  
Solvent: dmsd  
Data collected on: Jun 22 2012

Sample #45, Operator: nanir

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 2.500 sec  
Width 8000.0 Hz  
16 repetitions  
OBSERVE H1, 499.7151049 MHz  
DATA PROCESSING  
Line broadening 0.2 Hz  
FT size 65536  
Total time 1 min 12 sec



Plotname: --Not assigned--

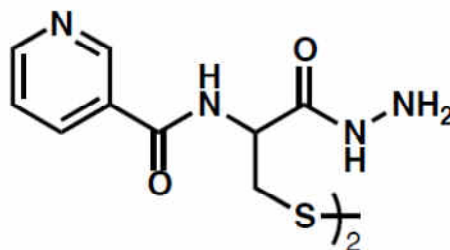
**Fig. S3** NMR spectra of cystine dihydrazide nicotinamide

Sample Name:  
KJ-4-117-13C  
Data Collected on:  
indy.caltech.edu-inova500  
Archive directory:  
/home/nanir/vnmrsys/data  
Sample directory:  
KJ-4-117-13C  
FidFile: CARBON01

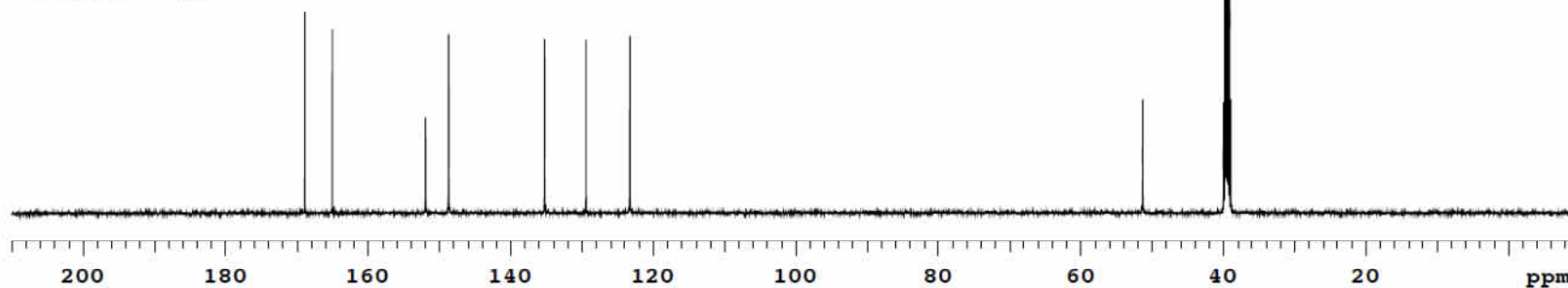
Pulse Sequence: CARBON (s2pul)  
Solvent: dmsd  
Data collected on: Jun 22 2012

Sample #39, Operator: nanir

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.400 sec  
Width 31446.5 Hz  
1000 repetitions  
OBSERVE C13, 125.6535178 MHz  
DECOUPLE H1, 499.7176040 MHz  
Power 39 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 40 min



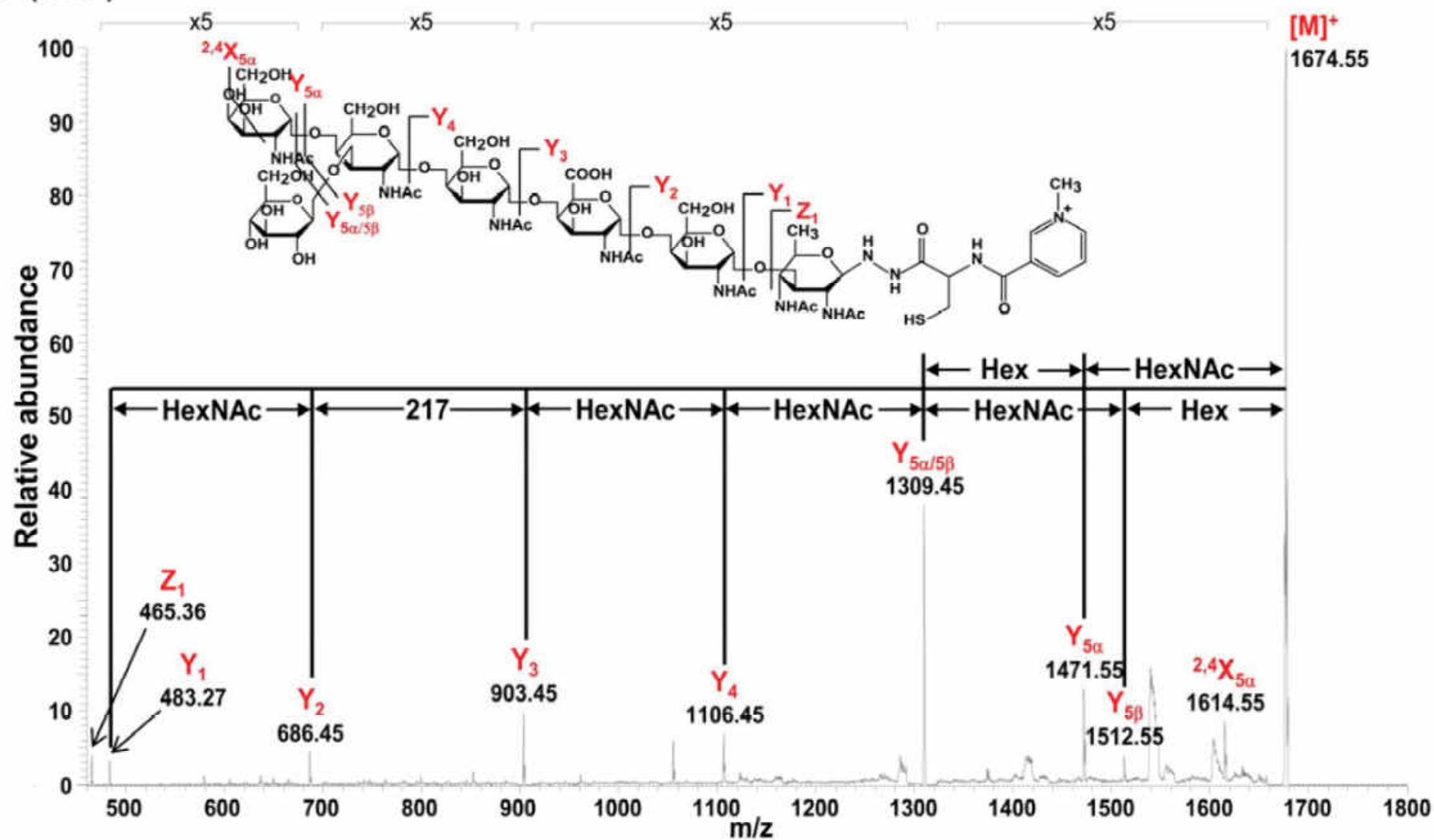
6



Plotname: --Not assigned--

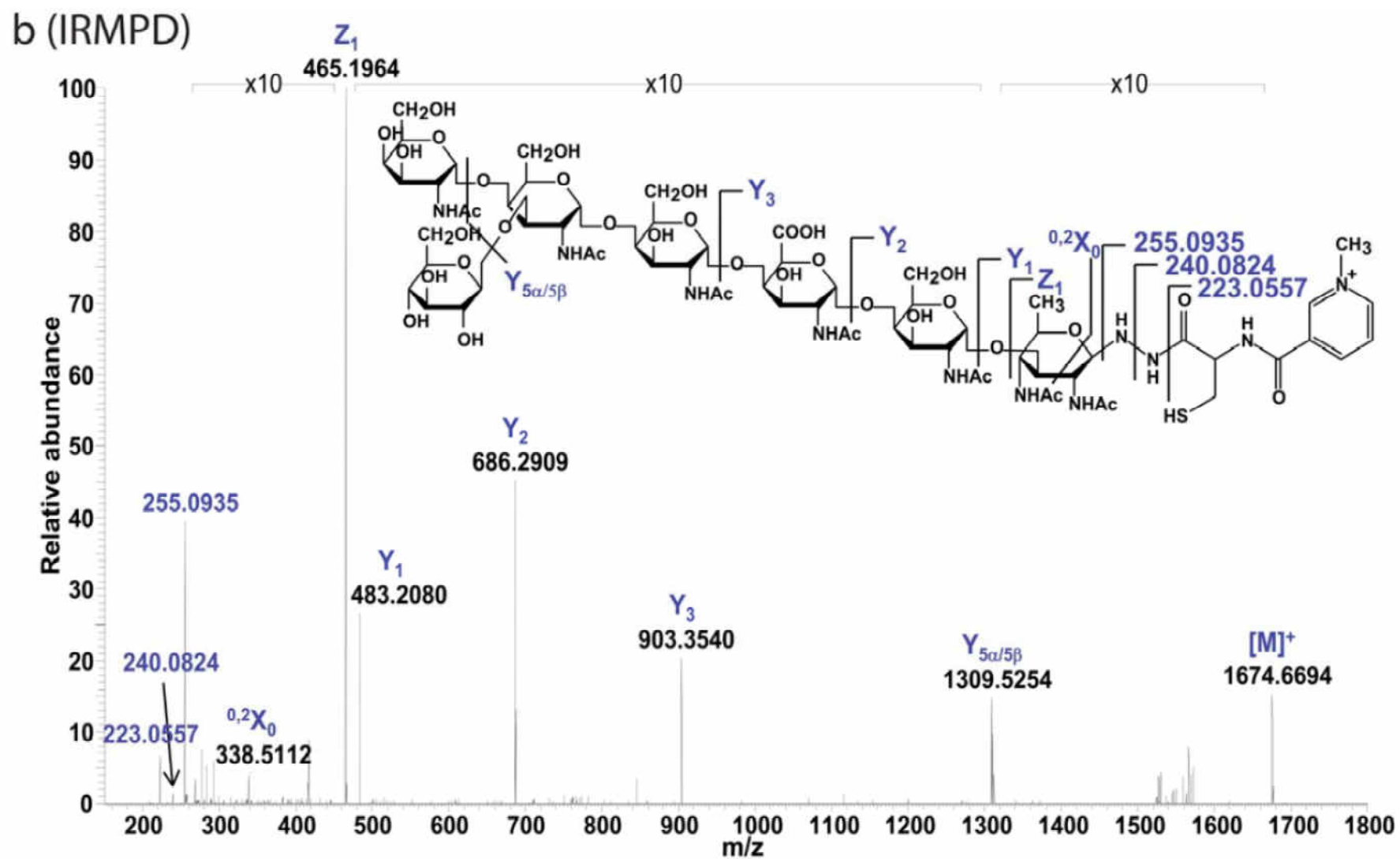
**Fig. S3** (continued) NMR spectra of cystine dihydrazide nicotinamide

a (CID)



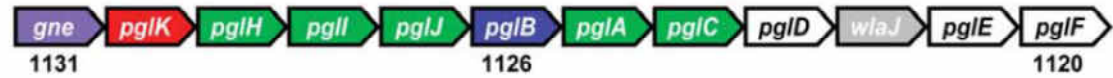
**Fig. S4** Selected tandem MS spectra of the  $fOS_{CC}$ . (a) CID (30-ms with 15% collision energy)



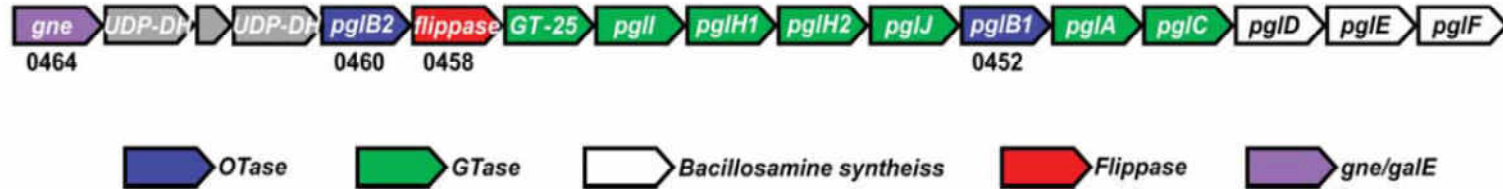


**Fig. S4** (continued) Selected tandem MS spectra of the fOSC<sub>c</sub>. (b) IRMPD (50-ms with 10-W laser power) MS/MS spectra

*C. jejuni* NCTC11168



*C. concisus* RM5485



**Fig. S5** Selected bacterial protein N-glycosylation (*pgl*) gene clusters. Blue, oligosaccharyltransferase gene (*pglB*); red, flippase gene (*pglK*); green, glycosyltransferase (GT) gene; purple, UDP-sugar epimerase gene (*gne* or *galE*); white, sugar biosynthesis gene. GT-25, group 25 family glycosyltransferase; UDP-DH, UDP-sugar dehydrogenase.